

# PATENT SPECIFICATION

(11) 1319 236

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NO DRAWINGS

- (21) Application No. 44362/69 (22) Filed 8 Sept. 1969  
 (21) Application No. 14583/70 (22) Filed 25 March 1970  
 (23) Complete Specification filed 1 Sept. 1970  
 (44) Complete Specification published 6 June 1973  
 (51) International Classification B29D 7/02, 27/00; B01D 13/04  
 (52) Index at acceptance  
 B5B 230 283 35Y 360 365 369 412 426 794  
 B1X 6



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(54) DESALINATION

(71) We, UNITED KINGDOM ATOMIC ENERGY AUTHORITY of London, a British Authority, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the treatment of liquids by reverse osmosis, and to perm-selective membranes of copolymers which are useful for such treatments. These perm-selective membranes are useful for desalination, and the recovery of substantially pure water from brackish or impure water or from aqueous solutions of sodium chloride, and also for the treatment of other aqueous and non-aqueous liquid feedstocks.

It is known that certain specialised membranes consisting of polymeric materials, notably cellulose acetate membranes with a heterogeneous, partly porous, essentially low-density structure with a high-density skin, have the property of removing certain ions from aqueous solutions when the solution in contact with the membranes is subjected to a hydrostatic pressure considerably in excess of the osmotic pressure. With suitable membranes the flux of water through the membrane in such conditions can be very greatly in excess of the salt flux. The effect is that salt is excluded from the water passing through the membrane and the solution on the high pressure side becomes more concentrated. The salt rejection efficiency varies with membrane material and structure. With the best heterogeneous cellulose acetate membranes operated in ideal conditions, the percentage rejections may be as high as 99% of the original salt content. However, the disadvantages of such membranes are that their preparation is complicated, they have to be kept wet and cannot therefore be dried for transport and handling, they are not very strong, their fine structure and performance can be affected by the high hydrostatic pressures to which they are subjected in operation, and they are sensitive to

chemical and biological reagents and influences which attack cellulose acetate.

The present invention provides in one aspect a perm-selective membrane of a copolymer derived from three or more co-polymerisable monomers having ethylenic unsaturation and containing units derived from:—

- (i) a styrene or an alkyl- or aryl-substituted styrene,
- (ii) a saturated or unsaturated alkyl or aryl acrylate or alkacrylate,
- (iii) an  $\alpha$ -unsaturated carboxylic acid or anhydride,

in which the molar proportion of (i):(ii) is from 4:1, to 1:4, and the molar proportion of (i) + (ii):(iii) is from 4:1 to 1:4.

While membranes having special shapes and configurations, e.g. bundles of hollow fibres, are included in this invention, the membrane will generally be a flat film such as may be obtained, for example, by casting a solution of the polymer on a sheet of glass. The membranes of this invention may be either homogeneous or heterogeneous, heterogeneous porous or spongy membranes may be prepared by methods analogous to those used by Loeb and Sourirajan in respect of cellulose acetate. Homogeneous dense membranes are advantageous in respect of their generally greater strength and chemical resistance and their more constant desalination performance.

The term "dense membranes" in the present context means a membrane with a density substantially the same as the density of its constituent polymer material, i.e., containing no pores or voids other than the micro voids of the type normally expected to be present in the polymer structure.

The copolymers constituting the membranes for use in the process of the invention are preferably random copolymers produced from three or more ethylenically unsaturated monomers. The monomers are so selected that with each there is associated one or more of the

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three properties: hydrophobicity, hydrophilicity (with the possibility of hydrogen bonding) and chemical reactivity (of the type to permit easy cross-linking in the final polymer). These particular properties in the monomers may be associated with either the general structure of the monomer unit or with the presence of particular functional groups therein, or both. Some of the structures or functional groups may combine two functions (e.g., hydrophilic nature with reaction facility for cross-linking of the ultimate polymer). Generally, the hydrophilic monomer is a monomer which produces a water-soluble or water-sensitive polymer on homopolymerisation. A difficulty in ascribing certain properties to the monomer on the basis of the structure of the side groups, is that in cases when several groups with conflicting properties are present, the effect of certain groups may be much more pronounced than others. Methacrylic acid is a good example, where the effect of the methyl group (hydrophobic) is quite negligible compared with the hydrophilic carboxylic group.

The above functions of the individual monomers are incorporated in the resulting copolymer.

As stated above, the copolymers of which the membranes of this invention are made are derived from at least one monomer from each of three classes.

(i) The first class includes styrene and alkyl- and aryl-substituted styrenes. The substituent may be on the aromatic ring or on the side chain. Preferred substituents are methyl and phenyl groups. The preferred compound is unsubstituted styrene.

(ii) The second class includes butadiene and saturated and unsaturated alkyl and aryl acrylates and alkacrylates. Among these acrylic esters, we prefer to use saturated and unsaturated lower alkyl acrylates and methacrylates, e.g. methyl, ethyl and allyl acrylate and methacrylate.

The alkyl and aryl substituents which may be present in the monomers in classes (i) and (ii) are principally included to provide hydrophobic sites in the polymer molecules. It will therefore be appreciated that their precise nature is not critical to this invention.

(iii) The third class of monomers is intended to provide hydrophilic sites in the polymer molecules and includes  $\alpha$ -unsaturated carboxylic acids and anhydrides. Preferred compounds are maleic anhydride, acrylic acid and methacrylic acid.

In addition to having hydrophilic and hydrophobic sites, the polymer molecules (if they are not already cross-linked) must also have sites of chemical reactivity of the type to permit cross-linking of the polymer. These sites are normally provided by the carboxylic acid groups of the class (iii) monomers, but more may also be present if butadiene or an unsaturated alkyl acrylate is used as the class

(ii) monomer.

In order to yield membranes having useful combinations of strength and flexibility, the molar ratio of class (i) monomers to class (ii) monomers in the polymer must be from 4:1 to 1:4.

In order to yield membranes having useful combinations of water flux and salt rejection, the molar ratio of hydrophobic monomers from classes (i) and (ii) to hydrophilic monomers from class (iii) must be from 4:1 to 1:4, preferably from 2:1 to 1:2.

Polymers in the class described above have properties which make them interesting for use as perm-selective membranes. However, the variation of perm-selective properties among polymers within this class is substantial. The mechanisms by which reverse osmosis operates are not clearly understood, and correspondingly it is not possible to predict with confidence whether one polymer will provide a better perm-selective membrane than another. Consequently, a certain amount of experimentation is unavoidable for anyone who wishes to prepare a membrane having an optimised combination of properties for a particular purpose.

It is also advantageous that the molecular weight of the copolymers should be high. Most of the polymers resulting from the above system are soluble in dimethylformamide (DMF) and it is, therefore, convenient to relate the desirable molecular weight to solution viscosity in this solvent. On this basis the relative viscosity of a 0.2% solution of the polymer in dimethylformamide at 30°C. should preferably be higher than 1.2.

The unexpected discovery that, with polymers of the type described, desalination performance is frequently improved by increasing the molecular weight, suggests that the beneficial effects of cross-linking in this respect may also be, at least in part, due to the effective overall molecular weight increase. It is, therefore, not practicable to suggest an effective limit for the desirable molecular weight.

The copolymers can be prepared by free radical copolymerisation. This can be carried out, as most appropriate to the specific monomer system used, in bulk or in solution or aqueous emulsion, in the absence of air (or oxygen) and in the presence of a compound capable of forming free radical fragments on thermal homolytic scission, such as benzoyl peroxide or azo-diisobutyronitrile (AZDN). The copolymer can be isolated and purified by the appropriate well-known methods, e.g., solvent/non-solvent precipitation or steam distillation, followed by washing and drying. In most cases, it is preferable to carry out the reaction in solution at 40–70°C., with 0.1% AZDN, to 20–50% conversion, and to precipitate the copolymer with a non-solvent, e.g., petroleum ether. It will be understood that

not only the random copolymers but also block or graft copolymers of the general type described may be of use as the constituent materials of the membranes used in the process of the invention. Such block or graft copolymers can be prepared by methods known in the art.

Membranes for use in improved process may be conveniently prepared from the copolymers by simple casting from a solution in a suitable solvent. The casting may be by means of a doctor knife, or spin casting or other known methods. The conventional doctor knife casting technique is quite suitable for membranes down to about 0.1 microns in thickness. Suitable solutions may contain 0.1 to 50% w/w, preferably 10 to 20% w/w, of the copolymer in a solvent. Most of the copolymers are soluble in tetrahydrofuran (THF). The casting may be carried out on a polished glass plate under controlled temperature and humidity conditions and the resulting membranes may be dried first in air and then in vacuo at 30–40°C. (in the case of THF) for 24 hours or longer before removal from the plate. The removal of solvent may be assisted by immersion in cold water, in which case a final drying step will be necessary to remove the water.

Membranes having appropriate combinations of water flux and salt rejection properties are generally constituted by films having an effective thickness of from 0.1 to 50 microns. The membrane may take the form of a homogeneous dense film having a thickness of from 0.2 to 5.0 microns. Or the membrane may take the form of a heterogeneous partly porous film having a dense skin of a thickness (the effective thickness) of from 0.2 to 5.0 microns. When the membrane takes the form of a bundle of hollow fibres, the wall thickness of the fibres is generally from 4.0 to 20 microns. Thicker films than these can appropriately be used to test the properties of the polymer, but are unlikely to be commercially attractive.

The films may also be formed by special techniques *in situ* in the desalination apparatus (e.g., inside tubes). In such cases the film would still be formed from a solution of the polymer, but the actual application technique would have to be suited to the nature and form of the surface on which the film is to be deposited.

It is also possible to prepare a composite membrane from a mixture of two or more of the copolymers, each individual polymeric component having functional hydrophilic groups of a different kind. If, in a composite membrane prepared from a mixture of two copolymers, one of the copolymers contains acidic groups (e.g., carboxylic groups) and the other contains basic groups (e.g., amine or pyridine groups), then a membrane may be produced from the mixture which will, at least in part, represent a "polysalt" formed by

mutual neutralisation by the appropriate groups of one copolymer of the groups of the other copolymer. The composite membrane may be formed by, e.g., casting from a single solution of the "polysalt", or by consecutive castings from solutions of the two copolymers. Composite membranes of this type can be chemically neutral, exhibiting little or no tendency to combine with ions present in the solutions undergoing desalination.

We have referred above in particular to membranes which were homogeneous and dense, and we have particularly described the preparation and use of unsupported homogeneous dense membranes.

To be of commercial use, membranes need to be very thin (in the case of homogeneous membranes) or to have a very thin effective surface layer (in the case of asymmetric membranes such as those prepared by Loeb). As stated above, useful membranes are likely to be from 0.2 to 5.0 microns in thickness. Homogeneous dense membranes which are thin enough to provide commercially attractive flux rates may—especially for the purposes of handling and prolonged use—benefit from being combined with a suitable porous support. This should be sufficiently permeable not to impair the flux but strong enough to support the membrane. Suitable surface characteristics to provide the right degree of adhesion if the membrane is cast *in situ* on the support are also desirable.

Membranes may also be produced in asymmetric forms from the polymers of the invention. In one version the procedure can be analogous to that used in the preparation of some asymmetric cellulose acetate membranes, i.e., with the aid of a suitably selected multi-solvent system. When cast under appropriate conditions the solution of the polymers of the invention in such a system can produce a membrane having a comparatively porous "spongy" layer and comparatively dense thin "skin". Asymmetric membranes produced in this way and form also have certain uses, but the preparation technique is usually complicated.

In yet another variant of the production of an asymmetric membrane structure, the membrane may originally be produced in porous form—e.g. by the inclusion and subsequent removal of a water-soluble porosity-inducing agent, or by other means known in the art—and a surface "skin" may then be formed on one side by "glazing" through brief exposure to the action of a suitable solvent or heat or both.

Alternatively again, the membrane may be deposited in homogeneous form on a porous substrate. Suitable substrates are resin-coated paper and cellulose triacetate films. This arrangement has the advantage that the membrane itself may be as thin as is desired without putting the strength of the product at risk.

After-treatment of the membranes may be carried out by applying, to the previously produced membrane, a solution of a reagent capable of reacting with functional groups of the copolymer. If the solution of the reagent is applied to the surface of the membrane and the time and conditions of treatment are suitably regulated, the reaction may be confined substantially to the membrane surface. Impregnation of the membrane with the solution of the reagent in association with appropriate time and other conditions of treatment, can lead to reaction throughout the membrane. Examples of reagents suitable for after-treatment of some of the copolymers described are:— alkaline, earth chlorides, mono- and di-amines, ammonia and other basic compounds. A cross-linking agent may be used so as to effect cross-linking of the copolymer in the membrane. These can conveniently be applied in the form of aqueous solutions to the copolymer membrane, with a view to reaction with hydrophilic acid groups contained therein or on the surface thereof.

Both for desalination and other separation the membrane may advantageously be treated (by immersion or by contact with at least one face thereof) with a 0.1% to 10% w/v aqueous solution of hexamethylene diamine for a period of from 5 seconds to 120 minutes, shorter contact times generally being appropriate for more concentrated solutions. It is also advantageous to heat the treated membrane at a temperature of from 100°C. to 200°C. for from 5 to 120 minutes, shorter heating times being appropriate at higher temperatures.

Surprisingly, it has been discovered that this treatment can improve both the salt rejection properties and the "pure" water flux through the copolymer membrane. In membranes produced from copolymers containing unsaturated functional groups (e.g., the allyl group), cross-linking of the copolymer of the membrane (either on the surface or throughout the structure) can also be effected via such groups. Insoluble and highly chemically resistant membranes (or membranes with insoluble surface layers) with improved salt rejection properties, can be produced in this way from the copolymers described above.

Reagents which can be used to cross-link the polymer (and especially also to increase its molecular weight) are certain polyamides of the Versamid type, for example, those sold under the Trade Marks Versamid 100 and Versamid 115, certain epoxy compounds and di- or poly-isocyanates. It may be advantageous, from the point of view of not impairing and even of improving the flexibility of the membrane, to use comparatively long chain cross-linking agents, for example, certain commercially available epoxide resins, e.g., those sold under the Trade Mark Epikote 828.

Thus, a solution of the polymer (preferably in tetrahydrofuran) may be mixed in the de-

sired stoichiometric proportions (for example 20:1 free acid groups:epoxy groups) with a solution in the same solvent of an epoxide resin. A film cast from this mixture is subsequently heated (e.g. at 150°C. for 30 minutes) whereby chemical reaction occurs between the polymer and the epoxide resin.

Di- and poly-isocyanates may be used in a similar way, and have the advantage that heating of the membrane is unnecessary as reaction takes place at ambient temperatures. Excessive heating of the membrane is liable to cause damage. Suitable di-isocyanates include toluene di-isocyanate and 4,4' - di - isocyanate - diphenylmethane.

A major use for the membranes described above is in desalination. However, these membranes are also capable of separating water from aqueous solutions of other solutes, both ionic and non-ionic, including alcohols, esters, organic acids, proteins, and sugars. Such processes may alternatively be regarded as ones for concentrating the aqueous solution, and may find commercial application in the food industries. For example, beer may be concentrated with the aid of these membranes.

Another possible use of the membranes is in effluent purification.

Furthermore, these membranes may be used in separation processes involving non-aqueous media, particularly organic liquids. Thus, for example, petroleum fractions may be separated by reverse osmosis. These membranes have the advantage over cellulose acetate films, where separations involving organic solvents are concerned, of not swelling or being soluble in the organic solvents. This is particularly true when the polymer making up the membrane is cross-linked, e.g., by the hexamethylene diamine after-treatment described above. In organic separations of this kind, it seems likely that the hydrophilic groups on the polymer of the membrane act as organophobic groups, and the hydrophobic groups as organophilic groups.

The invention thus includes a process for the treatment of a liquid feedstock, which process comprises bringing the liquid feedstock into contact with a membrane as hereinbefore defined and applying pressure to the liquid feedstock in contact with the membrane, whereby a liquid, of different composition to the liquid feedstock passes through the membrane.

The feed stock may be an aqueous solution of one or more metal salts and the liquid which passes through the membrane is substantially pure water. Alternatively the feed stock may be an aqueous one containing dissolved or suspended organic matter which is retained by the membrane.

In its specific application to desalination, the present invention provides a process for the desalination of water by reverse osmosis, which process is characterised by the use of the mem-

branes described above. The process may be effected under conventional conditions, for example, using a hydrostatic pressure of from  $1.4 \times 10^5$  to  $1.05 \times 10^5$  kg/m<sup>2</sup>. If the initial salt concentration of the water to be purified is high, or if the salt rejection of the membrane is low, it may be desirable to pass the water through several membranes in succession. The membrane, hydrostatic pressure and other conditions should be chosen to provide a water flux of at least 2.4, preferably at least 4.0 litres per square metre per day, with at least 40%, preferably at least 60%, salt rejection.

The following Examples illustrate the invention. Relative viscosities are of a 0.2% solution of the polymer in DMF at 30°C.

The film thicknesses of the membranes used in these examples varies from 14 to 61 microns, and the perm-selective properties of the membranes are determined in relation to a 0.05N solution of sodium chloride. These are convenient parameters to choose in order to test the properties of the polymer of which the membrane is made. When a polymer having a particularly attractive combination of properties is found, membranes for commercial use (and such use is by no means limited to desalination) would normally be made at substantially lower film thicknesses of the order of 0.2 to 5.0 microns. The manufacture of such thinner membranes presents no additional difficulty, however.

#### Example 1

A mixture of methylmethacrylate—1 mole, styrene—1 mole, and methacrylic acid—1 mole, was heated with 0.1% w/w of AZDN, under air-free conditions, at 70°C. for 24 hours. The clear, hard, solid polymer which was obtained was comminuted on a laboratory mill to a fine powder and heated under vacuum at 50—60°C. to remove the last traces of residual monomers. The terpolymer had a relative viscosity of 1.51.

A film was cast from 15% w/v solution of this terpolymer in THF on to a glass plate using a doctor knife, and dried at 35°C. for 24 hours and then at 30°C. under vacuum for a further 24 hours.

The clear homogeneous film (16 microns thick), when tested in a reverse osmosis rig under pressure of  $3.5 \times 10^5$  kg/m<sup>2</sup> of 0.05N solution of sodium chloride, showed a water flux of the order of 2.4 litre/metre<sup>2</sup>/day and 40% desalination. It showed no change or degradation after 120 hours, under these conditions.

#### Example 2

The monomer/catalyst mixture of Example 1 was heated with an equal weight of tetrahydrofuran at 50°C. for 5½ hours under nitrogen.

The polymer was precipitated by adding the product to 5 volume of methanol/water (4:1 w/v). The solid terpolymer was filtered

off, washed and dried. It was found to have a relative viscosity of 1.25, and acid content of 25% (expressed as methacrylic acid).

A 15 micron thick film was prepared from 10% w/v solution of the above terpolymer in THF by the technique of Example 1. When tested in the reverse osmosis rig, under  $7 \times 10^5$  kg/m<sup>2</sup> pressure of 0.05N solution of sodium chloride, the film gave a water flux of 20 litres/metre<sup>2</sup>/day and up to 90% desalination.

#### Example 3

The monomer/catalyst mixture of Example 1 was heated with an equal weight of acetone, under nitrogen, at 40°C. for 48 hours.

The very viscous solution which was obtained was diluted with half its volume of THF and the polymer was precipitated in 3 volumes of petroleum ether (B.P. 40—60°C.). The terpolymer was washed and dried as before. It was found to contain 47.3 mole % acid (as methacrylic acid) and a relative viscosity of 2.23.

A 15 micron thick film of this terpolymer cast from a 15% w/v solution in THF, gave a water flux of 36 to 112 litres/metre<sup>2</sup>/day and up to 86% desalination under reverse osmosis conditions using  $7 \times 10^5$  kg/m<sup>2</sup> pressure of 0.05N solution of sodium chloride.

#### Example 4

The monomer/solvent/catalyst mixture of Example 3 was heated under nitrogen at 70°C. for 3½ hours.

After working up as in Example 3, the terpolymer was found to contain 36.7% of combined acid, but its molecular weight was considerably lower than the Example 3 polymer as shown by a relative viscosity of 1.14.

A 15 micron thick film of this terpolymer prepared by casting as in Example 1 showed a variable water flux of 4 to 40 litre/metre<sup>2</sup>/day and only 20—30% desalination using  $7 \times 10^5$  kg/m<sup>2</sup> pressure of 0.05 N sodium chloride solution. However, after being immersed in a 1% w/v aqueous solution of hexamethylene diamine for 5 minutes followed by water washing and heating at 100°C for 1 hour, the film showed a water flux of 280—320 litres/metre<sup>2</sup>/day and 70% desalination, under the same conditions.

#### Example 5

An equimolar mixture of styrene, allyl methacrylate and methacrylic acid was heated in equal weight of acetone with 0.1% w/v AZDN at 70°C for 3½ hours, under nitrogen. The polymer had a relative viscosity of 1.23. The polymer was worked up as in Example 3 and a 15 micron film cast from a 15% solution of the terpolymer in THF (with 1.5% benzoyl peroxide dissolved therein) was dried as usual and then heated at 100°C for 2 hours. The crosslinked terpolymer gave a water flux of 480—800 litres/metre<sup>2</sup>/day and about 30% desalination under  $7 \times 10^5$  kg/m<sup>2</sup> pressure of 0.05 N sodium chloride solution.

## Example 6

5 An equimolar mixture of methylmethacrylate, styrene and methacrylic acid was heated under nitrogen gas with 0.1% of AZDN and in solution in an equal weight of acetone at 40° C. for 78 hours.

10 Benzene was then added to the resultant viscous solution in an amount equal by weight to the original weight of the acetone. The terpolymer was precipitated by pouring this mixture into a large excess of petroleum ether (B.P. 40—60°C.). The polymer, in the form of a fibrous solid, was filtered off, washed with petroleum ether and dried in a vacuum oven at 60°C. for 6 hours. The yield of the polymer was 17.5% by weight of the original monomer mixture.

20 The dry polymer was extracted twice with diethyl ether in a Soxhlet extractor and redried. It was found to contain 35.5% w/w of combined methacrylic acid and its relative viscosity in DMF was 1.60.

25 A film was cast by the usual method from a 20% w/v solution of this terpolymer in tetrahydrofuran, and dried in air for 8 minutes, then for 2 hours at 35°C. followed by vacuum drying at 35°C. for a further 24 hours. The film was clear and strong, approximately 27 to 30 microns thick.

30 When tested under reverse osmosis conditions at  $7 \times 10^5$  kg/m<sup>2</sup> of 0.05N sodium chloride solution, the film gave water flux of 1.6—2.4 litres/metre<sup>2</sup>/day and desalination of 35%. However, after immersing the film in 1% w/v aqueous solution of hexamethylene

diamine for 5 minutes and washing off the excess of the reagent, the water flux, under the same conditions, was found to be in the region of 152—268 litres/metre<sup>2</sup>/day and the salt rejection of the film was increased to 82%. The treated terpolymer film was subjected to these conditions for 65 hours and showed little or no change in its properties after this time.

## Examples 7 to 14

45 The properties of further copolymer membranes are given in Table 1 below. In Examples 7 to 13, the copolymer was prepared by bulk polymerization in a sealed tube (using the molar ratios given) with 0.1% w/w AZDN at 70°C. for 24 hours. The product was comminuted and heated under vacuum to remove any residual monomers.

50 In Example 14, the copolymer was prepared by emulsion polymerisation in a glass vessel under nitrogen using ammonium persulphate (1% of the total weight of the monomers) and "Empicol" (Registered Trade Mark) LX emulsifier (3% of the total weight of the monomers), at 80°C. for 19 hours. The residual monomers were removed by steam distillation. The product was coagulated, washed and dried.

60 In the Table, the following abbreviations appear. ST (styrene); MMA (methyl methacrylate); MANH (maleic anhydride); EA (ethyl acrylate); AA (acrylic acid); BD (butadiene). Reverse osmosis was  $7 \times 10^5$  kg/m<sup>2</sup> of 0.05N sodium chloride solution.

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TABLE I  
Copolymer Membranes Tested in Reverse Osmosis

Example No.	Copolymer	Relative Viscosity	Casting Solution	Membrane thickness	Reverse osmosis		Stability of Membrane
					Flux l/m <sup>2</sup> /day	Desalination	
7	ST:MMA:MANH 1 : 1 : 1	1.24	15% Acetone/ DMF	25 $\mu$	216 — 180	63%	Satisfactory after 100 hours
8	ST:MMA:MANH 1 : 1 : 2	1.24	25% Acetone	19 $\mu$	28	80%	Swelling after 100 hours otherwise satisfactory
9	ST:MMA:MANH $\frac{1}{2}$ : $\frac{1}{2}$ : 1	1.45	20% Acetone	16 $\mu$	1.6 — 44	up to 84%	Swelling after 70 hours, otherwise satisfactory
10	ST:EA:MANH 1 : 1 : 2	1.32	15% Acetone	14 $\mu$	56	75%	Satisfactory
11	ST:EA:MANH $\frac{1}{2}$ : $\frac{1}{2}$ : 1	1.38	25% Acetone	15 $\mu$	140 — 160	75%	—
12	ST:MMA:AA 1 : 1 : 2	2.10	15% THF	15 $\mu$	0.8 — 36	80 — 91%	Swollen after 52 hours otherwise satisfactory
13	ST:BD:AA 1 : 1 : 1	1.18	25% Acetone	18 $\mu$	8 — 200	up to 66%	Swollen after 60 hours otherwise satisfactory
14	ST:EA:AA 1 : 1 : 1	>1.2	15% Acetone	38 $\mu$	1.04	62%	Satisfactory after 70 hours

## Examples 15 to 23.

These Examples illustrate after-treatments using hexamethylene diamine.

- 5 Terpolymer membranes (1:1:1 molar styrene/methyl methacrylate/methacrylic acid) were immersed in aqueous solutions of hexamethylene diamine under nitrogen at ambient temperature. The treated membranes were drained of excess reagent and then thoroughly
- 10 rinsed in distilled water. Following heating in an oven (if given) the membranes were re-soaked in distilled water and tested under reverse osmosis conditions viz. under a pressure

of  $7 \times 10^5$  kg/m<sup>2</sup> of 0.05N solution of sodium chloride. Results are given in Table 2 below, 15 in which:

D = Duration of test in hours.

F = Flux in litres per square metre per day

%R = Percent rejection defined as

$$\frac{[\text{NaCl}]_{\text{input}} - [\text{NaCl}]_{\text{output}}}{[\text{NaCl}]_{\text{input}}} \times 100 \quad 20$$

TABLE 2

Example	Nature of film (where treated, 0.5% wv/ HMD used)	Thickness of films tested min/max. microns	D	F	%R
15	Untreated 'control' film	30.4 — 33.0	200	0.068— 0.104	62
16	Film treated at ambient tempera- ture for 5 mins. only.	30.4 — 35.6	200	16	81
17	Film treated at ambient tempera- ture for 15 mins. followed by oven heating 100°C./ 1 hour	27.9 — 55.8	120	60	84 — 85
18	As 17 but no sub- sequent heating	25.4 — 61.0	120	300— 256	66 — 64
19	Film treated at ambient tempera- ture for 30 mins. only	35.6 — 45.7	100	360— 320	61 — 56
20	Film treated at ambient tempera- ture for 60 mins. only	33.0 — 50.8	100	272	66 — 59
21	Film treated with 0.1% HMD for 60 minutes	25.4 — 30.4	65	11.2	82 — 71
22	Film treated with 1.0% HMD for 5 minutes	40.6 — 48.3	65	268— 152	81 — 79
23	Film treated with 1.0% HMD for 60 minutes	22.9 — 35.6	65	1080— 880	52



The relative viscosity of the polymer from which the film were made for Examples 15—23 (i.e., before HMD treatment) was 1.60.

- 5 In general, polymers used to form films without subsequent treatment should preferably have a relative viscosity of at least 1.20; polymers for use in films which are to be treated, e.g. with HMD, may have relative viscosities of at least 1.12.

10 WHAT WE CLAIM IS:—

1. A perm-selective membrane of a copolymer derived from three or more co-polymerisable monomers having ethylenic unsaturation and containing units derived from:—

- 15 (i) styrene or an alkyl- or aryl-substituted styrene,  
(ii) a saturated or unsaturated alkyl or aryl acrylate or alkacrylate,  
20 (iii) an  $\alpha$ -unsaturated carboxylic acid or anhydride in which the molar proportion of (i): (ii) is from 4:1 to 1:4, and the molar proportion of (i) + (ii): (iii) is from 4:1 to 1:4.

- 25 2. A perm-selective membrane as claimed in claim 1, wherein the monomers from which the polymer is derived are

- 30 (i) styrene,  
(ii) butadiene or methyl, ethyl or allyl acrylate or methacrylate,  
(iii) maleic anhydride or acrylic acid or methacrylic acid.

- 35 3. A perm-selective membrane as claimed in claim 1 or claim 2, wherein the polymer is a random copolymer.

4. A perm-selective membrane as claimed in any one of claims 1 to 3, wherein the polymer is a random terpolymer of styrene, methyl methacrylate and methacrylic acid.

- 40 5. A perm-selective membrane as claimed in any one of claims 1 to 4, wherein the polymer of which the membrane is formed has a relative viscosity, in a 0.2% solution in dimethylformamide at 30°C. of greater than 1.2.

- 45 6. A perm-selective membrane as claimed in any one of claims 1 to 5, having an effective thickness of 0.1 to 50 microns.

- 50 7. A perm-selective membrane as claimed in claim 5 in the form of a homogeneous dense film having a thickness of from 0.2 to 5.0 micron or of a heterogeneous partly porous film having a dense skin of a thickness of from 0.2 to 5.0 micron.

- 55 8. A perm-selective membrane as claimed in any one of claims 1 to 7, wherein the membrane has been treated with a 0.1% to 10% w/v aqueous solution of hexamethylene di-

amine for a period of from 5 seconds to 120 minutes.

9. A perm-selective membrane as claimed in claim 8, which, after treatment with the hexamethylene diamine solution, has been heated at a temperature of from 100°C. to 200°C. for from 5 to 120 minutes. 60

10. A perm-selective membrane as claimed in any one of claims 1 to 9, wherein the vinyl polymer has been cross-linked by having been admixed, in the form of a solution prior to membrane formation, with a solution of a polyamide, an epoxy resin, or a di- or polyisocyanate, which has been subsequently caused to react with and cross-link the polymer. 65

11. A perm-selective membrane as claimed in any one of claims 1 to 10 and substantially as hereinbefore described in any one of Examples 1 to 14. 70

12. A perm-selective membrane as claimed in any one of claims 1 to 10 and substantially as hereinbefore described in any one of Examples 15 to 23. 75

13. A process for the treatment of a liquid feedstock, which process comprises applying pressure to the feedstock in contact with a perm-selective membrane as claimed in any one of claims 1 to 12, whereby a liquid of different composition to the feedstock passes through the membrane. 80

14. A process as claimed in claim 13, wherein the liquid feedstock is an aqueous solution of one or more metal salts and the liquid which passes through the membrane is substantially pure water. 85

15. A process as claimed in claim 13, wherein the liquid feedstock is an aqueous one containing dissolved or suspended organic matter which is retained by the membrane. 90

16. A process as claimed in claim 13, wherein the liquid feedstock is non-aqueous. 95

17. A process for the desalination of water by reverse osmosis, which process is characterised by the use of a membrane as claimed in any one of claims 1 to 12. 100

18. A process as claimed in claim 17 and substantially as hereinbefore described in any one of Examples 1 to 14. 105

19. A process as claimed in claim 17 and substantially as hereinbefore described in any one of Examples 15 to 23.

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